

On the Conversion of Chlorine into Hydrochloric Acid, as observed in the Deposition of Gold from its Solutions by Charcoal. By Wm. Morris Davis.

(Read before the American Philosophical Society, April 6, 1883.)

The simple fact of such conversion, while of interest in a chemical point of view, would not justify me in occupying the time of this meeting in discussing it.

But in its technical application to the cheap and effective deposition of gold from its solution, both from the novelty and usefulness of the method it is deemed worthy of your attention.

Preliminary to the description of the process, and necessary to an appreciation of its value in a technical sense, the following facts have an important bearing.

It has been estimated that only about one-tenth of the gold of our country exists in an uncombined state (as free milling ores), or as dust and grains of gold in river sands, or placer washings; such gold is largely obtained by amalgamation processes.

The remaining nine-tenths is found in veins of the older geologic period, and is held in combination by sulphides, arsenides and tellurides; to these ores the process of amalgamation with mercury has been found inapplicable; hence they are generally known as refractory ores.

Two methods have been adopted for working these refractory ores, viz.: Smelting or fusion with lead, and chlorination; that is by first reducing the combined sulphides, &c., to oxides, and then dissolving the gold by means of chlorine.

The process of smelting is applicable to refractory ores only, when they carry a high value in gold, because of the high cost attending the method. Crooks and Röhrig's "Metallurgy" teaches that "ores containing combined gold to the amount at \$20 per ton cannot be profitably fused with lead; even could they be raised without mining cost." As a rule in this country this process is not applied on ores below the value of \$40 per ton.

By chlorination, ores carrying \$20 per ton, can be profitably worked, mining costs included.

Without entering into the question of chlorination, it may be remarked that various methods have been devised whereby the solvent powers of chlorine have been applied to the extraction of gold from such ores. The process is an old one, is one which has been long in use, and the excellence of the method is admitted; it has been found that the solvent power of a chlorine solution is much increased by operating with the gas under a pressure equal to two or more atmospheres.

By such proceeding it is evident that the chlorine solution employed in the chlorinating apparatus will be highly saturated with the gas; it was with such supercharged solutions that the following experiments with carbon were conducted. It is taught that water at ordinary temperatures will

hold in solution two and a half times its volume of chlorine, and that five cubic feet of the gas will weigh one pound, and it has been found in practice that under the Mears' system or method, by pressure, the resultant solution carried such volume of gas as to require an excessive amount of sulphate of iron, or sulphuretted hydrogen (where these precipitants are used) to neutralize the excess of chlorine, before they could act in precipitation of the gold. Thus adding a cost that our low grade ores will not bear; other difficulties and shortcomings, attend the precipitations by these reagents, not necessary to describe, as they are well known to all who have adventured on any of the various modes of chlorination, and which are clearly set forth in Crook and Röhrig's "Metallurgy," in describing Plattner's Chlorinating works at Richenstein, upper Silesia.

From the unsatisfactory results of thus precipitating the gold after it is obtained in solution, chlorination processes have been of limited application, being mainly confined to operations on a small scale and to the concentrated tailings of other processes.

In the effort to overcome these obstacles to success, and to adapt chlorination to the requirements of enlarged operations, the writer reached results which are herein described and explained.

In an aqueous terchloride, or normal solution of chloride of gold, very many substances, both inorganic and organic, will decompose the salt and precipitate the gold in a metallic state, or in combination with the substances employed; but excepting the proto-sulphate of iron, or sulphuretted hydrogen, they are quite inapplicable in a solution surcharged with chlorine, especially is this the case, in the use of organic substances, owing in a measure to their rapid decomposition and disintegration by chlorine.

In vegetable charcoal we find an organic structure capable of resisting the destructive influences of chlorine, therefore, after numerous failures with other organic substances, this was adopted as subject of experiment; and it was found possessed of a remarkable power in decomposing the auric solution, converting the chlorine rapidly into ClH , depositing the gold upon, and throughout the charcoal, and allowing contained copper to pass off in the escaping fluid. Thus, by a simple regulated flow through charcoal, surmounting the sole difficulty to the employment of the chlorine process, on an extended scale of operations.

The gold was retained in metallic form, and of great purity; by long continued action the gold was observed to replace the wasting carbon, atom for atom, fibre for fibre, retaining the form and structure of the fragment of coal, so that on the dissipation of the carbon by incineration, and washing away the ash by SO_3 , a brilliant and perfect golden pseudomorph of the coal was obtained.

The copper in the solution was not affected by the coal, and it passed to its appropriate tank to be precipitated by iron as cement copper.

In a report made by Prof. F. M. Endlich, to parties in New York, he says, "In order to test the efficacy of the process, I took, systematically,

samples from the receiving tanks, from the collecting tanks, from the pipe which carried the solution to the filter, and from the stop cock through which the liquid passed after the solution had been in contact with the charcoal.

"The unvarying results of these repeated tests may be summed up briefly:

"While I never failed to get copious precipitates of gold from the solution in the tanks, and from that taken from the faucet through which it flowed into the filter, I never obtained the slightest gold precipitate from *the same liquid after it had passed through the charcoal.*

"The tests which were employed to detect gold in the liquid which had passed through the charcoal were varied, and entirely sufficient to be convincing. Sulphate of iron will decidedly indicate the presence of one part of gold to forty thousand parts of liquid.

"Neither with this reagent, nor with any others that were used could a trace of gold be detected in the liquid taken from the lower spigot of the first barrel, containing one hundred pounds of charcoal, measuring twenty-eight inches vertically, after about nine hundred and sixty gallons of terchloride solution had passed through it."

This amount of solution represented about six thousand pounds of ore, carrying according to assays, \$72 in gold.

He continues, "Briefly restating what has been said at greater length, I would repeat that the charcoal filter as here used, is entirely sufficient to precipitate from a terchloride solution, *all the gold* contained therein."

Prof. Endlich remarked on the disappearance of the chlorine from the solution after it had passed the filter. At this stage of the experiment the true cause of the deposition of the gold was not determined, on this point he writes :

"As to the chemical exchanges which take place, and produce the result, I cannot speak positively, and have not, at present, the time at my command to make the requisite investigations."*

It was not until operations were conducted on an enlarged scale that we arrived at an explanation of the reactions which occur in the contact of the terchloride solution with carbon.

It was known to a few antiquarian delvers in chemical records, that among the multitude of substances which decompose a solution of chloride of gold, carbon was named by Count Rumford as possessing this property, but it was only under certain conditions that he observed it to act, for he says, "recently ignited charcoal separates gold, only in sunshine or at 109°;" further experiment proved that under the influence of light, or heat, gold will separate from its solution in the absence of charcoal.

Thus Kane teaches that, "when chlorine water is exposed to the light, it is gradually decomposed, chloride of hydrogen being formed, and

*Prof. E. subsequently writes: "Your conclusions regarding the decomposition of water for the formation of ClH seem a little forced."

oxygen being set free, he further states that heat has the effect of decomposing such solution with the same results;" should gold be present, it will be precipitated in proportion to the disappearance of free chlorine.*

When it thus appeared that the recited conditions alone were sufficient for the deposition of gold from its solution, then was Rumford's discovery consigned to the limbus of useless speculations. This remarkable property of carbon is casually mentioned by a few authors; but it is nowhere taught that carbon is distinguished by any remarkable energy, or as differing from the crowd of organic substances with which it was classed.

Neither is it anywhere suggested that such deposition was of any commercial value, and no use has ever before been made in the metallurgic separation of gold from its solution, nor has carbon been employed in obtaining gold from its ores except as a fuel.

Just the opposite has been the case, for when the attention of experts was called to the claims of this process, they generally agreed that there was nothing in chemical laws or scientific principles to sustain the assumption, and at this moment well informed minds are at a loss to account for the remarkable energy of this new agent in reducing gold from a solution to a metallic state, and the additional fact, that it is inert towards other earthy and metallic constituents of the solution. Thus serving as a refining agent also.

As sustaining the claim of *novelty*, for the hypothesis of the conversion of chlorine into ClH , by carbon, allusion may be made to the contrary opinion of many chemists, as expressed in correspondence with the writer. Several incline to the opinion that the reduction is simply a mechanical attraction of the carbon for the gold (corresponding to the action of animal carbon on the impurities in sugar); this opinion has been held regardless of the disappearance of large volumes of chlorine, and the formation of its equivalent of ClH .

Others ascribe the action to the defective carbonization of the wood, and seek explanation in the "oils, resins, or partially changed wood fibre," which are known to precipitate gold.

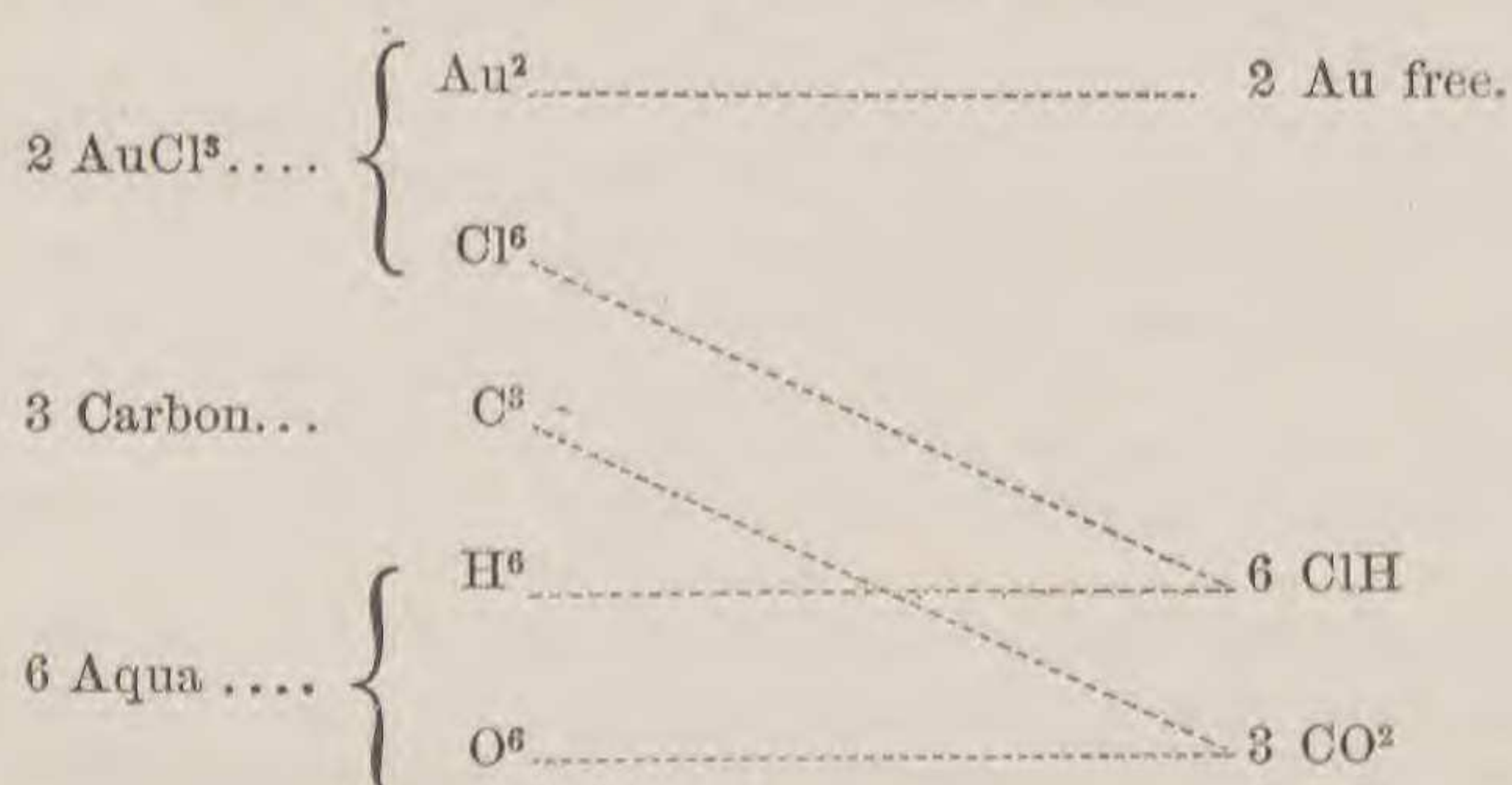
Some claim that the action is due to the presence of hydrogen in the gaseous ammonia, which charcoal absorbs with avidity from the air. If such were the case, the action would be of short duration in the presence of highly charged chlorine solutions; but, that such is not the case, may be experimentally shown, by submitting a perfectly prepared piece of charcoal to a high heat, and, while in a state of ignition, quenching it in distilled water (simply for the purpose of cooling), then immediately transfer it in the dark to a cold surcharged chlorine solution carrying gold and copper; the effect will be the disappearance of the free chlorine, the

* In the quantitative investigation of this subject by Dr. G. A. Koenig of the Pennsylvania University, as published in *Journal of Franklin Institute*, May 8, 1882, this property of heat, to decompose a gold solution was overlooked, and his conclusions are invalidated by his employing heat in the digestion of the carbon in the gold solution.

presence of its due equivalent of ClH , the deposition of the gold on the carbon, while the copper will be found in the solution. That the action of carbon in effecting such changes is not evanescent has been shown, but may be repeated in brief :

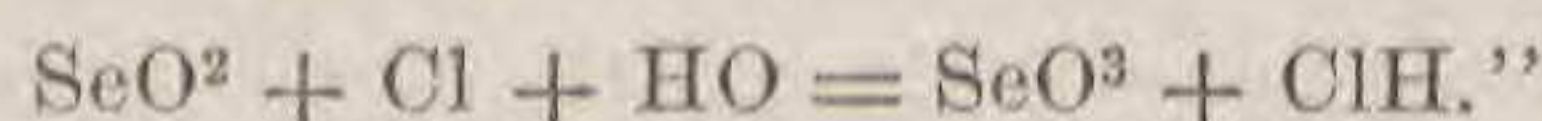
A filter containing one hundred and sixty pounds of charcoal in the operations of the mill, after a continuous flow of chlorine solution for ten days, and passing sixteen thousand gallons (representing eighty tons of ore) was still effective in producing the above results. Some few writers in their hasty experiments failed in getting satisfactory results and dismissed the subject as "the wild dream of a mad inventor."

The following formula is offered as explanatory of the reactions attending the deposition of gold from its solution by charcoal :



Chemistry teaches that "Chlorine has a powerful affinity for hydrogen, and when brought in contact with other bodies, in the presence of water, will decompose the water by combining with the hydrogen forming ClH and liberating oxygen. Thus, substances are frequently oxidized by chlorine to a higher degree than by nitric acid. Kane teaches that

"Selenious acid (SeO^2) and chlorine in the presence of water is converted into selenic acid (SeO^3) and hydrochloric acid (ClH).



Reasoning from analogy, we may explain the reactions in the deposition of gold : by substituting carbon for selenious acid in this formula ; in which case the carbon is oxidized at the expense of the water, the hydrogen uniting with the chlorine to form ClH .

That such are the reactions may be assumed, *a priori*, as all the elements involved are satisfied according to their equivalent affinities, and form definite compounds, leaving the gold free ; and it follows, that the deposition of the gold is occasioned by the conversion of the chlorine (which is a solvent of the metal) into chlorohydric acid (in which gold is insoluble), and it is in nowise owing to an attraction or affinity of carbon for gold.

As copper is soluble in muriatic acid it is not affected by the change in

the condition of the chlorine, from a free to a combined state, and this metal remains in solution, as does every contained substance, which is soluble in ClH .

That the free chlorine is thus converted into the combined state is shown by the following experiment, which was made after the carbon had converted two hundred times its volume of chlorine, or the filter of 80 gallons of coal had received 8750 gallons of the chlorine solution, carrying about twice its volume of gas :

Of the running solution two samples were taken, one from the surface before it entered the coal, the other from the bottom after it had passed through the filter ; from the first, the chlorine acted powerfully on the senses ; in the second, no odor was perceptible.

To equal portions of the two samples were added nitrate of silver, the precipitated chloride was collected, washed and dried with due precautions, and the weights of the two precipitates exactly corresponded ; the one measuring the sensible, the other the combined chlorine.

In only one experiment of long-continued action, has a sensible diminution of the carbon been observed ; further and more exact determinations than could be made in a mine laboratory are required to establish this point.

Neither has it been determined to what extent the deposit of gold can be carried by this method, the button of gold now exhibited weighing eighteen and a half pennyweights was recovered from the ash of two ounces of charcoal ; the filter from which it was taken seemed to have lost none of its activity. The grains from the surface of this filter yielded the pseudomorphs of gold which are before you, and the weight of the gold is above one-third the weight of carbon, which has been removed.

As affecting this question, and possibly of interest to the chemist, the following observation was made on the action of dilute SO^3 on charcoal taken from a filter after being subjected to the action of chlorine for six days :

With the thought that washing this carbon with dilute SO^3 might clean the coal and increase its activity, a portion of it was placed in a glass percolating tube, and the above acid passed slowly through it. The solution from the bottom came away of a dark brown color, but retaining its transparency ; on passing this through filtering paper no deposit was retained, showing that the color was not owing to dust of the coal. The solvent action of the acid continued as long as it was applied, and until the size of the carbon grains were sensibly diminished, when the acid solution was replaced by a current of cold water. Now the escaping fluid was almost black, being many shades darker than the acid solution. This when largely diluted was of a rich brown color, and perfectly transparent. The carbon grains were rapidly diminishing in size, and seemingly entirely soluble, when the process was interrupted to test the power of the remaining contents of the tube on an auric chlorine solution.

On passing such solution through the residuum, it was found to have

lost all power in converting the chlorine or depositing the gold. Although the coal in the large filter from which this portion was taken, retained its full power for three succeeding days, and, so far as the eye could judge its character as a charcoal, remained unchanged; whilst the portion subjected to SO^3 had lost all characteristics of charcoal in qualities and appearance. Pressing occupations interfered with a further examination of this method of reducing charcoal to a soluble condition. This is presented as a new and interesting feature in the history of chlorine.

From notes of a laboratory experiment in a qualitative examination, the following details are given as illustrative of the methods employed to arrive at reliable results. The novelty of the subject and the importance of the conclusions, are offered as apology for the minuteness of detail:

A glass percolator, 18 inches deep, was filled with granular wood charcoal, without other preparation than expelling enclosed gases, and removing adhering substances by immersion in water; a gum tube and compressor at the outlet served to regulate the flow; twenty-four ounces of coal were employed; 100 gallons of solution were used, carrying chlorine that was evident to the senses in escaping fumes; inhalation could not be made at the surface of the coal. This represented 750 pounds of an ore assaying \$15.65 gold to the ton. Temperature of the room about 75°F. , density of the liquid 3.75 Beaumé; the rate of flow was regulated to one gallon per hour, and continued uninterrupted until the close of the experiment, or 100 hours.

At intervals of an hour samples of the escaping fluid were taken, and tested for gold with sulphate of iron, in every instance it failed to detect gold.

The rich blue color of the escaping liquid showed the presence of copper; remembering that the presence of copper had hitherto impaired the action of sulphate of iron as a precipitant, it remained to be shown that the want of precipitate in the test tubes was a reliable indication of the absence of gold; to test this, every tenth gallon of the filtrate was subjected to the following treatment:

The copper was precipitated by clean iron wire, the resulting cement copper washed on a filter, then dissolved by SO^3 , and the undissolved portions secured on a filter, dried, and incinerated, and the ash assayed for gold; the return of which was .01 grain. Now as one gallon represented the $\frac{1}{266}$ part of a ton of ore, the above result shows a loss by reason of the presence of copper of 2.66 grains of gold per ton = $11\frac{1}{2}$ cts.

At the conclusion of the flow, the charcoal was washed, carefully incinerated in an iron dish, and the ash smelted with borax. The button of gold weighed 139 grains, as the return from 750 lbs. of ore; which is equal to 371 grs. @ $4\frac{1}{4}$ cts. \$15.77 per ton.

Assay value of the ore 15.65 " "

A difference of 12 cents per ton in favor of the finer determinations of analysis by solution, over the approximative method of smelting by fire assay.

Working on a larger scale, the following result was arrived at, in the chlorination works near Salisbury, N. C. :

1963 tons worked ; average assay.....	\$6.11	=	\$11,994.19
Net returns from U. S. Mint.....	gold	=	11,158.82
			<hr/>
			\$835.37

Which shows a loss in working equal 43 cents per ton.

By careful and constant assays of the spent sands, this loss is accounted for, by the washing in the leaching tanks being arrested before the last traces of gold were removed. To thoroughly wash these sands would require a large volume of water, and the loss is regarded as an economic waste.

On this point Dr. Jno. F. Boynton, in a report on an experimental test of the process, reports :

"The spent ores, or tailings, as found in the leaching vats after washing, were subjected to rigid examination ; samples were taken of each charge, and careful fire assays made, and in no case did an ounce assay afford gold equal to the one-thousandth part of a grain."

Without entering into the technical details or the costs of manipulation, the above results are presented as evidence that the refractory ores of gold may be worked on an enlarged scale by the joint chlorine and carbon processes, and may in the end utilize the vast stores of these ores, which lie useless in our Southern and Western gold fields.

Stated Meeting, May 4, 1883.

Present, 13 members.

President, Mr. FRALEY, in the Chair.

Letters accepting membership were received from Prof. Heilprin, dated Academy Natural Sciences, Philadelphia, April 4; Mr. A. E. Lehman, dated 907 Walnut street, Philadelphia, April 30, 1883; Mr. Philip C. Garrett, dated Fairfield, Germantown, Philadelphia, May 3, 1883, and Mr. Dillwyn Parrish, dated Philadelphia, May 5, 1883.

Letters of acknowledgment were received from the Verein für Erdkunde, at Dresden (108); and the Accademia dei Lincei at Rome (109, 110, 111).